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Nodules of Diagenetic
Barite in Upper Devonian
Shales of Western New York

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Nodules of Diagenetic Barite in Upper Devonian Shales of Western New York

By JAMES F. PEPPER, SANDRA H. B. CLARK,
and WALLACE DE WITT, JR.

A description of the character, geologic setting,
and possible origin of barite nodules near
Silver Creek, Chautauqua County, N.Y.

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DEPARTMENT OF THE INTERIOR
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PREFACE

The manuscript for this report was nearly completed by James Pepper when he died in 1963. That same year, it was partly rewritten by Wallace de Witt, Jr., who had worked with him in the field, but it was not published. Because descriptions of diagenetic barite rosettes and nodules in New York State have never been published, I have reworked the manuscript for publication as a bulletin. I revised and deleted to reflect new concepts and terminology, but adhered as closely as possible to Pepper's observations and interpretations.

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September 7, 1984



CONTENTS

Preface	III
Abstract	1
Introduction	1
Character of the barite nodules	2
Geologic setting of the barite nodules	5
Origin of the barite nodules	9
References cited	10

FIGURES

1. Map showing locations of the village of Silver Creek, where the barite nodules described in this report were collected, and places in New York where other types of barite have been found 2
2. Photograph of natural sections of two barite rosettes in a very dark gray mudrock in the bed of Walnut Creek showing the radial structure common to these nodules 4
3. Photograph of a natural section of a cephalopod from the *Manticoceras* zone along Walnut Creek showing crystals of barite in the chambers of the shell and rosettes of barite in the enclosing rock 5
4. Generalized columnar section showing the stratigraphic positions of zones of barite nodules in the lower part of the Java Formation along Walnut Creek 6
5. Map showing the area of occurrence of barite nodules near the village of Silver Creek 7
6. Photograph of an irregularly shaped coalesced calcareous nodule from the Hanover Shale Member on Walnut Creek showing pockmarks where the included barite rosettes have been partly etched by weathering 8
7. Photograph of a shell of a fossilized cephalopod from the *Manticoceras* zone along Walnut Creek showing barite rosettes on the shell 9

TABLE

1. Reported occurrences of barite in New York 3

Nodules of Diagenetic Barite in Upper Devonian Shales of Western New York

By James F. Pepper,¹ Sandra H. B. Clark, and Wallace de Witt, Jr.

Abstract

Barite nodules are present in the basal part of the Hanover Shale Member of the Java Formation of Late Devonian age near the village of Silver Creek, Chautauqua County, New York. Many nodules are spherulitic and consist of acicular bladed crystals oriented radially to a small mass of equant barite crystals at the center of the nodule; these nodules are also called rosettes. The nodules from near Silver Creek are diagenetic, whereas other forms of barite reported to exist in the sedimentary rocks of the State are replacement deposits or fill pre-existing voids. The internal structure of the rosettes and their relation to the enclosing strata suggest that the radial crystals grew from a central core or nucleus in a gel-like clay ooze on the sea floor. The nodules appear to have formed a few inches below the water-sediment interface during deposition of the enclosing strata and during the primary expulsion of water from the mud. Most probably the nodules grew in a low-energy environment in a protected embayment seaward of the growing Catskill delta at or below effective wave base.

INTRODUCTION

Although barite is not a commonly recognized constituent of sedimentary rocks, it occurs sparingly at many places in New York in sedimentary rocks as well as in igneous and metamorphic rocks (fig. 1, table 1). In the Adirondack Mountains in the northeastern part of the State, many small veins containing barite are known in both igneous and metamorphic rocks of Middle Proterozoic age and in the bordering sedimentary strata of Late Cambrian and Ordovician age. Barite in the sedimentary rocks commonly is present in veins, vugs, and geodes, and at some places, it forms irregular masses associated with dolo-

mite and celestite. In addition to the occurrences in the eastern part of the State, barite has been observed in geodes in Silurian strata near Rochester and in the vein filling of septaria near Auburn, Buffalo, and Laona. Fossils partly replaced by barite were described by Clarke (1904, p. 332, 336, 400, 430-436) as being from the vicinity of Java Village, Wyoming County, and from the area between the village of Naples and Honeoye Lake in southern Ontario County. Martens (1925) noted the presence of barite in septaria of Middle Devonian age in the vicinity of Cayuga and Seneca Lakes in the central part of the State. In most of the occurrences of barite in New York, the barite appears to replace some primary constituent of the rock or to fill pre-existing voids.

Unlike barite in other areas of New York, barite near the village of Silver Creek, town of Hanover, Chautauqua County, is present as spheroidal nodules whose internal structure and relation to the enclosing strata suggest that they are diagenetic. During mapping in 1947 and 1951, many ellipsoidal to spheroidal barite nodules and rosettes were collected from the gray mudrock and black shale in the basal 27 feet of the Hanover Shale Member of the Java Formation in the canyons of Silver Creek and Walnut Creek in northeastern Chautauqua County. The barite rosettes show a spherulitic structure of acicular bladed crystals oriented radially to a small cluster of equant barite grains at the center of the nodule (fig. 2). Their structure differs from the homogeneous internal structure of most of the calcareous nodules and concretions that are abundant in the Upper Devonian strata of western New York. Although barite rosettes and nodules are common in other States, for example, in important commercial deposits of barite in Nevada and Arkansas, nodules or rosettes have not been described from the barite occurrences in New York State. In this report, these unusual barite nodules and rosettes and their geologic setting are described and an origin is suggested.

¹Deceased.

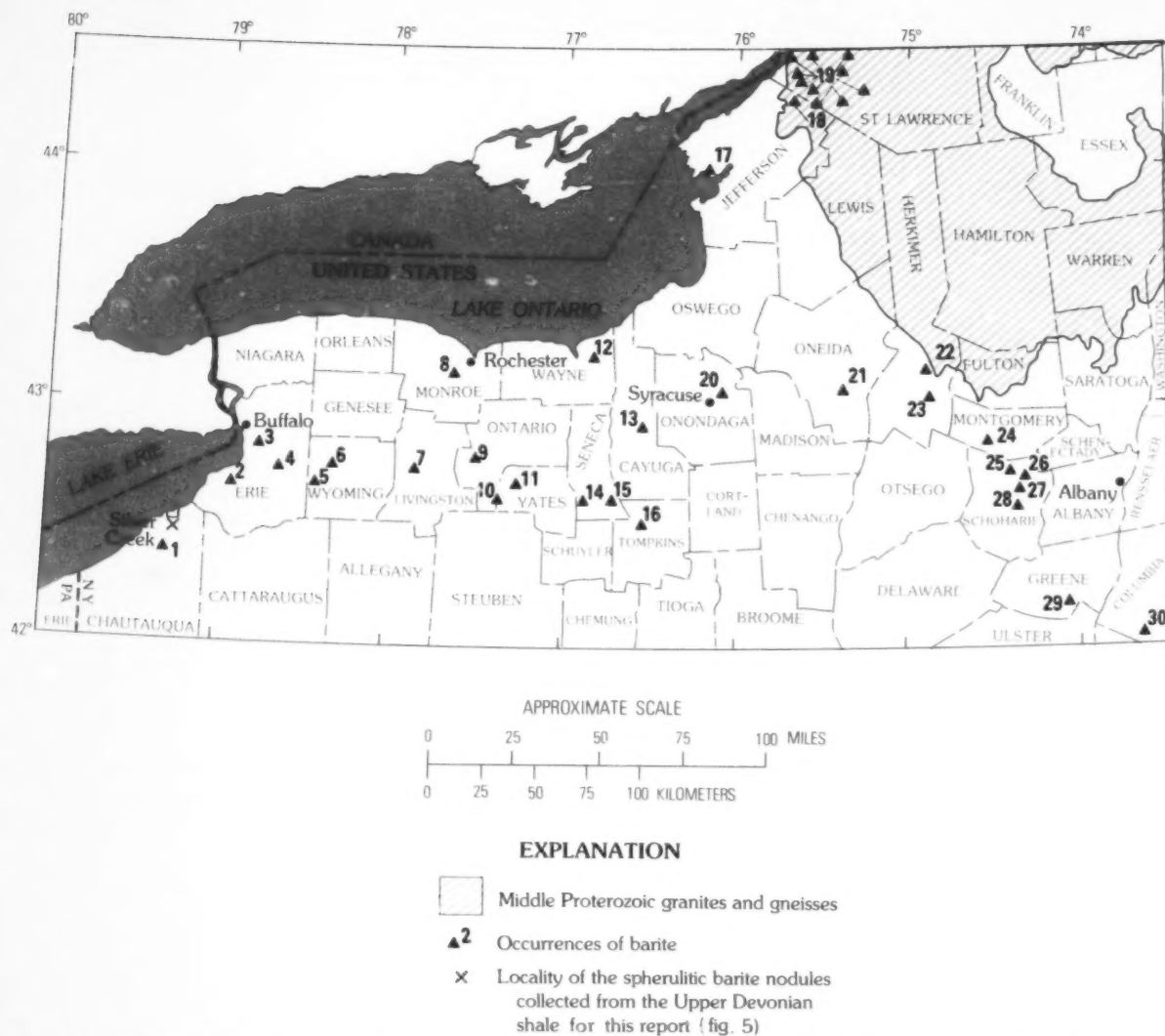


Figure 1. Map showing locations of the village of Silver Creek, where the barite nodules described in this report were collected, and places in New York where other types of barite have been found. Table 1 lists the reports describing barite at each numbered locality.

CHARACTER OF THE BARITE NODULES

Most of the barite in gray mudrock occurs in rosettes or nodules from $\frac{1}{8}$ inch to $1\frac{1}{2}$ inches in diameter. The nodules range from spheroidal to discoidal. Some barite is present in irregular masses of coalesced nodules as much as 3 inches thick and 8 to 10 inches long. An individual rosette consists of a small nucleus of white to light-gray granular barite surrounded by a radiating fringe of acicular, bladed crystals of white, light-yellow, light-gray, and light-brown barite. The bladed crystals, whose length is

commonly about eight times the diameter of the nucleus, have their long axes normal to the surface of the nodule (fig. 2). In cross section, a rosette has an appearance similar to that of a small chrysanthemum. The surface of the rosette is generally moderately pustulate and rough; the pustules correspond to the ends of the radiating crystals. Because the rosettes are generally coated by a film of unctuous light-gray clay, their radial structure is not generally apparent. The boundary of an individual nodule is sharply defined, particularly if the nodule was embedded in soft mudrock. However, the borders of adjacent nodules are indistinct and irregular in places where many

Table 1. Reported occurrences of barite in New York
[Do., ditto]

Map no. (fig. 1)	Location	References
1	Laona -----	Beck, 1842, p. 209.
2	Eightmile Creek -----	de Witt, 1956.
3	Buffalo -----	Beck, 1842, p. 209.
4	Cazenovia Creek -----	Pepper, de Witt, and Colton, 1956.
5	Java Village -----	Clarke, 1904, p. 336.
6	Varysburg -----	Wallace de Witt, Jr., unpub. data, 1984.
7	Nunda -----	Whitlock, 1903, p. 44-45.
8	Rochester -----	Beck, 1842, p. 206.
9	Honeoye Lake -----	Clarke, 1904, p. 332, 430-436.
10	Naples -----	Clarke, 1904, p. 400, 430.
11	Middlesex -----	Clarke, 1904, p. 434.
12	Wolcott -----	Beck, 1842, p. 209.
13	Auburn -----	Do.
14	Lodi -----	Martens, 1925.
15	Portland Point -----	Do.
16	Interlaken -----	Do.
17	Pillar Point -----	Beck, 1842, p. 206; Merrill, 1895, p. 582, 1904, p. 189; Newland, 1919, p. 33; Hough, 1850, p. 426.
18	Oxbow -----	Beck, 1842, p. 206.
19	St. Lawrence County, Rossie area	Brown, 1983; Beck, 1842, p. 208; Hough, 1850, p. 428; Whitlock, 1903, p. 74-89; Emmons, 1842, p. 341; Neumann, 1952; Newland, 1919, p. 34; Cushing and Newland, 1925, p. 82; Dana, 1892, p. 903.
20	Syracuse -----	Beck, 1842, p. 206; Merrill, 1904, p. 190.
21	Clinton -----	Dale, 1953, p. 77-79, 96.
22	Fairfield -----	Beck, 1842, p. 205; Newland, 1919, p. 34; Merrill, 1904, p. 189-190; Whitlock, 1903, p. 38-39.
23	Little Falls -----	Do.
24	Sprakers Basin -----	Whitlock, 1903, p. 46-47.
25	Carlisle -----	Grabau, 1906, p. 360; Newland, 1919, p. 34; Beck, 1842, p. 207.
26	Ball's Cave, strontium mine ---	Grabau, 1906, p. 357-361; Emmons, 1835, p. 182-183.
27	Schoharie -----	Grabau, 1906, p. 357-361; Merrill, 1904, p. 189; Shepard, 1835, p. 363-368.
28	Middleburg -----	Beck, 1842, p. 208.
29	Catskill -----	Do.
30	Ancram lead mine -----	Hartnagel and Broughton, 1951, p. 61; Beck, 1842, p. 45-46, 409; Mather, 1843, p. 498-500; Newland, 1919, p. 142-143; Peterson, 1950, p. 47.



Figure 2. Looking down at natural sections of two barite rosettes in a very dark gray mudrock in the bed of Walnut Creek showing the radial structure common to these nodules. The core around which the acicular crystals grew shows faintly in the rosette next to the hand lens. Note the curved trace fossils in the matrix. Hand lens is $\frac{3}{4}$ inch in diameter.

nodules grew in proximity or coalesced during growth. Commonly the core or nucleus of the nodule contains one or more well-crystallized cubes of pyrite. Some nodules now consist largely of pyrite, although their radial structure indicates that the pyrite probably replaced the barite of the original nodule. In one large calcareous concretion from the barite-bearing strata, which partly encloses a fossilized cephalopod 2 inches in diameter, barite is present in rosettes in the limestone and as short euhedral crystals in the chambers of the cephalopod (fig. 3).

Thin-section examination shows that the nuclei of many rosettes are made up of many small equant grains of gray barite. The wide variation of their extinction angles indicates that the nuclei are aggregates of unoriented crystals.

Barite nodules from the black shale differ from those in gray mudrock in the general lack of long acicular crystals. The nodules from the black shale are composed mainly of unoriented, irregularly shaped barite crystals. Pyrite is relatively more abun-

dant and commonly fills the voids between irregular barite crystals. Calcite, which is present in small amounts in most of the nodules in the gray mudrock, is usually absent from most of the nodules in the beds of black shale.

GEOLOGIC SETTING OF THE BARITE NODULES

The barite nodules occur in greatest numbers in the lower part of the Hanover Shale Member of the Java Formation in the canyons of Silver Creek and Walnut Creek near the village of Silver Creek in northeastern Chautauqua County. The nodule-bearing strata are better exposed and more accessible for study along Walnut Creek south of U.S. Highway 20 than in outcrops along Silver Creek, although barite nodules have been collected from both localities (figs. 4 and 5). Similar-appearing nodules of barite having a spherulitic structure are present locally in the South Wales Member of the overlying Perrysburg Formation in the valley of Walnut Creek, but they are less abundant than nodules in the Hanover Shale Member.

The rocks that compose the two members of the Java Formation—the Pipe Creek Shale Member and the Hanover Shale Member—are together about 100 feet thick in outcrops along Walnut Creek and dip south at approximately 40 feet per mile. The stratigraphy of these rocks was described in detail by Pepper and de Witt (1950). The Pipe Creek Shale Member consists of 2 feet of fissile grayish-black to olive-black shale, which lies unconformably on the medium-gray mudrock and shale of the Angola Shale Member of the West Falls Formation (Pepper, de Witt, and Colton, 1956). The upper boundary of the Pipe Creek Shale Member is transitional into the dark-gray shaly mudrock in the basal part of the Hanover Shale Member through an interval of about 4 inches in which black and dark-gray shale are intercalated.

The Hanover Shale Member is composed largely of medium-gray mudrock, which weathers shaly at some places and blocky at others. A few beds of gnarly-weathering, medium-greenish-gray calcareous mudrock as much as 2 feet thick are present in the upper half of the member. Beds of olive-black to grayish-black shale from an inch to a foot in thickness are common, particularly in the lower part of the member where the barite nodules are concentrated. Some beds of black shale and some of the dark-gray mudrock contain many short, slightly curved trace fossils of contrasting color (fig. 2). Calcareous nodules and concretions of various sizes and shapes from

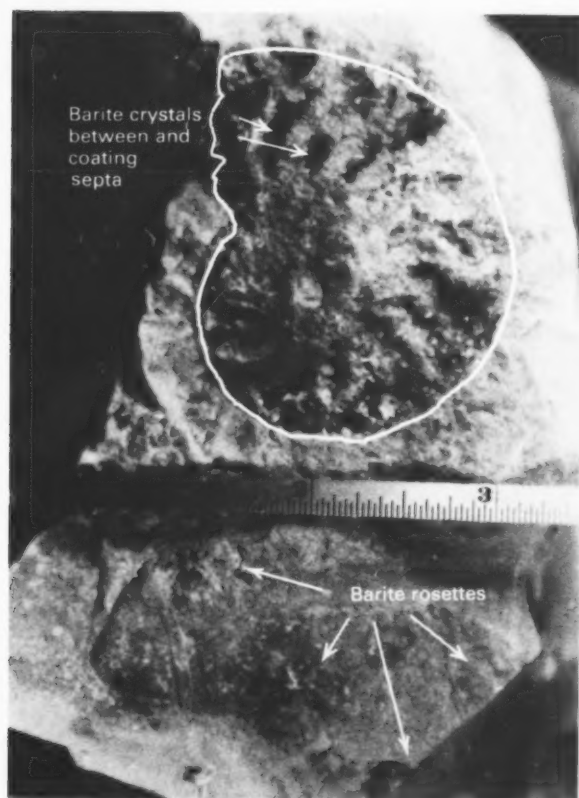


Figure 3. Natural section of a cephalopod from the *Manticoceras* zone along Walnut Creek showing crystals of barite in the chambers of the shell and rosettes of barite in the enclosing rock. Cephalopod is 2 inches in diameter.

SERIES	FORMATION	MEMBER	HEIGHT, IN FEET	LITHOLOGY	DESCRIPTION
UPPER DEVONIAN	JAVA FORMATION	HANOVER SHALE MEMBER	14		2-inch-thick zone of spheroidal calcareous nodules 1 inch in diameter
			13		Gray mudrock containing thin beds of black shale
			12		Calcareous nodules; some barite nodules Barite nodules in aggregates
			11		Black shale Gray mudrock containing much black shale Barite aggregates as wide as 4 inches; worm trails
			10		N-2 black shale; top contact gradational N-4 gray mudrock
			9		Black shale Gray mudrock Calcareous concretions; scattered barite nodules under the concretions
			8		Gray mudrock N-2.5 black shale N-4 gray mudrock Barite nodules 1 by 3 inches and aggregates of barite nodules
			7		N-2.5 black shale Gray mudrock Calcareous nodule 6 by 12 inches containing barite nodules
			6		Black shale; some barite nodules Gray mudrock Discoidal calcareous nodules 4 by 8 inches containing barite aggregates; <i>Manticoceras</i> sp.
			5		Black shale; some barite nodules N-3 dark-gray mudrock; barite nodules, some in aggregates
			4		Irregularly shaped calcareous nodules 3-4 by 10 inches; a few barite nodules on surface Gray mudrock Ramosse calcareous nodules 2 by 10 inches containing scattered barite nodules on surface
			3		A few barite nodules
			2		Gray mudrock
		PIPE CREEK SHALE MEMBER	1		Black shale

½ inch to 1 foot in thickness and from ½ inch to 2 feet in diameter are intercalated in the mudrock and shale of the member. Commonly the calcareous nod-

ules are concentrated in layers and zones, although at some places, they are scattered at random in the thicker layers of mudrock. A few beds of argillaceous limestone, as much as 1 foot thick, are present in the middle and upper parts of the Hanover Shale Member. Several of these beds of limestone appear to have formed by the coalescence of many calcareous nodules.

The barite nodules are present as isolated individuals or are concentrated in zones 1 to 4 inches thick in the lowermost 27 feet of the Hanover Shale Member. In the outcrops along Walnut Creek, the lowest zone of nodules is about 2 feet above the base of the Hanover Shale Member and about 4 feet above the base of the Java Formation (fig. 4). The greatest concentration of nodules is the interval from 6 to 16 feet above the base of the formation. Locally, the barite nodules are associated with nonbaritic calcareous nodules (fig. 6) and nodules, lumps, and irregular masses of brassy-yellow pyrite. Scattered barite nodules are present in beds of rusty-weathering black shale in the basal part of the member, but the shale contains fewer barite nodules than does the gray mudrock. The barite nodules commonly occur in a zone at the center of a discrete bed of mudrock or shale, whereas the calcareous nodules seem to be randomly distributed in a given bed. In several beds of gray mudrock, rosettes are associated with a large form of the cephalopod *Manticoceras* cf. *M. pattersoni*, which has been partly engulfed by very fine textured, slightly argillaceous calcareous nodules. In some specimens, the barite nodules occur partly within the shell wall of the fossilized cephalopods (figs. 3 and 7) and are, in turn, surrounded by the matrix of the enclosing calcareous nodule.

The structural attitude of the strata containing the barite nodules near the village of Silver Creek is simple. The rocks are on the gently dipping north-west limb of the Appalachian synclinorium, which is inclined to the south at about 40 feet per mile in this part of western New York. Locally, small noses and terraces are superimposed on the regional monocline. Exposures of the lower part of the Hanover Shale Member on Walnut Creek lie near the crest and on the northeast flank of a slightly asymmetric anticline whose axis trends about S. 30° E. (de Witt and Colton, 1953). The rocks in the area are cut by two well-defined sets of vertical joints that strike about N. 60° W. and N. 65° E. A less well defined and sparse set of joints ranging in strike from N. 10° W. to N. 20° W. is present locally. The joint surfaces are commonly tight and do not contain mineral filling or impregnations. The joints cut through the zones of nodules, but at no places are the nodules concentrated along

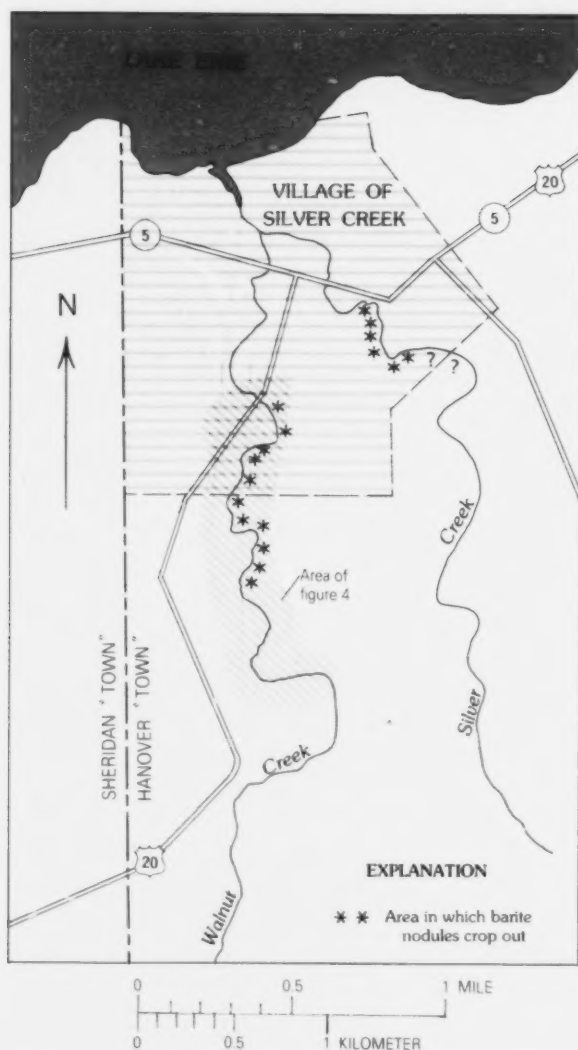


Figure 5. Map showing the area of occurrence of barite nodules near the village of Silver Creek. Sequence shown in figure 4 may be seen along Walnut Creek.

Figure 4. Generalized columnar section showing the stratigraphic positions of zones of barite nodules in the lower part of the Java Formation along Walnut Creek, town of Hanover, Chautauqua County. Numbers prefixed by "N" refer to the rock-color chart of Goddard and others (1948). See figure 5 for location of Walnut Creek and areas of outcrop.



8 Nodules of Diagenetic Barite in Upper Devonian Shales of Western New York

the joints or at the intersection of joints. The occurrence and spatial relationships show that the nodules formed before the joints.

Several small faults and folds are visible in the rocks of the Hanover Shale Member in the steep cliffs along Silver and Walnut Creeks. The folds are of low amplitude, commonly less than 5 feet. Both normal and high-angle reverse faults cut these Upper Devonian strata. The normal faults appear to be the result of gravity slumping of large joint blocks along the canyon walls. The reverse faults are high-angle thrusts dipping 55° to 80° to the northeast and striking on the average not far from N. 50° W., roughly parallel to the trend of the major joint systems. The



Figure 7. Shell of a fossilized cephalopod from the *Manticoceras* zone along Walnut Creek showing barite rosettes on the shell. Ruler is in inches.

Figure 6. An irregularly shaped coalesced calcareous nodule about 8 inches in diameter showing pockmarks where the included barite rosettes have been partly etched by weathering. The nodule is about 5.3 feet above the base of the Hanover Shale Member on Walnut Creek. Some pockmarks are highlighted by circles.

displacement, which is generally less than 5 feet at its maximum, can be seen to die out vertically both above and below the point of greatest offset. These faults appear to be relatively small features that do not cut through the entire sequence of Devonian strata. They may have formed during the Pleistocene as the result of the pressure of glacial ice, or they may have formed more recently as the load of ice was removed irregularly. Apparently the forces that locally produced faulting were taken up mainly by minor readjustments and bedding-plane slippage without faulting in most of the thick sequence of shaly Upper Devonian rocks. The small size and local nature of the faults suggest that they do not extend to great depth and that they probably do not penetrate the Proterozoic basement complex, which is about 4,000 feet below sea level in the Silver Creek quadrangle. Careful examination of fault surfaces failed to reveal traces of mineralization indicative of the upward circulation of hydrothermal solutions that might have introduced barium into the Hanover Shale Member after deposition. The absence of mineralization associated with the faults and joints and the absence of other phenomena, such as bleaching of rocks adjacent to fault surfaces, indicate that these rocks were not permeated by hydrothermal solutions after their deposition in Late Devonian time.

ORIGIN OF THE BARITE NODULES

The barite nodules in the Hanover Shale Member present two related questions: (1) What was the source of the barium? and (2) How did the nodules form?

One possible source of the barium that formed the barite nodules may have been pre-Devonian rocks that were exposed to erosion east and southeast of the Silver Creek area during Late Devonian time. At this time, the northern part of the Appalachian basin was partly covered by a shallow epicontinental sea into which the sediments of the great Catskill delta were being transported westward from source areas to the east and southeast. Freshwater mixed with the saline water of the epicontinental sea on the periphery of the Catskill delta, whose shoreline during Java time lay well southeast and east of the Silver Creek area. In the delta area, the coarser grained fraction of the stream-transported sediment accumulated near the shore along beaches and bars, whereas the finer grained components, mud and clay enriched in barium, were carried westward into a prodelta setting in western New York. The upper few feet of black and gray mud below the sea floor accumulated

in a low-energy, reducing environment and was most probably a gel-like ooze rich in organic material. In this euxinic environment, the barium could have remained in solution in the presence of dissolved hydrogen sulfide derived from decaying organic debris. When the hydrogen sulfide in the soft sediment had reacted with iron to form various sulfides of iron, small crystals of barite may have begun to grow in the relatively large volume of interstitial water trapped in the soft sediment just below the sediment-water interface.

The small semiequant crystals of barite in the cores of the nodules show much interference of crystals during growth of the nuclei of the nodules, suggesting that, at first, crystal growth was rapid from solutions nearly saturated with barium. Probably as the saturation decreased as these small crystals precipitated, the rate of crystal growth decreased, permitting the longer bladed crystals to form radially to the nucleus of the rosette. Small cubes of pyrite in the cores of some nodules suggest that the pyrite may have initiated the precipitation of the surrounding barite.

The presence of barite nodules on the shells of *Manticoceras* and in and on the surface of the surrounding dense carbonate nodules (figs. 3 and 7) indicates that the barite was precipitated in its present form at the time that the sediment was undergoing diagenesis. The presence of barite nodules associated with uncompact fossilized shells and adjacent to undistorted trace fossils (fig. 2) is strong evidence that the nodules formed while the enclosing mud was soft. Significantly, the largest carbonate nodules in the barite-nodule zone of the Hanover Shale Member on Walnut Creek are associated with a large form of cephalopod whose undeformed shells have the intraseptal cavities partly filled with barite crystals, indicating that the cephalopods were quickly enveloped by the calcium carbonate of the enclosing nodules before the delicate shell structure was crushed by the weight of accumulating sediment. The preservation of the undistorted fossils required the rapid protection of the enclosing nodules, and the ammonia released by the decomposing of the animal proteins may have increased the alkalinity of the water surrounding the animals to promote the deposition of the calcium carbonate in an environment in which the carbonate would not otherwise have precipitated. The barite nodules enclosed in the carbonate nodules are similar in size, shape, and form to the nodules in the main body of mudrock; this similarity shows that the growth of the barite nodules enclosed in carbonate nodules was complete before the carbonate nodules were formed, and that barite growth in general

was approximately coeval with carbonate growth. These data indicate an early genesis for the barite nodules.

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Pepper and others—NODULES OF DIAGENETIC BARITE IN UPPER D

